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X-RAY DIFFRACTION ANALYSIS OF PHASE FORMATION IN SYNTHESIS OF ACTINIDE MATRICES

S. V. Yudintsev,¹ S. V. Stefanovskii,² Ya. N. Jang,³ and S. Che³

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The products of synthesis of crystalline matrices promising for immobilization of actinides were studied by the method of x-ray phase analysis. The experiments were performed on compositions corresponding to the phase stoichiometry of structural types of zirconolite ($\text{CaZrTi}_2\text{O}_7$) and pyrochlore ($\text{CaCeTi}_2\text{O}_7$, $\text{Gd}_2\text{Ti}_2\text{O}_7$, $\text{Gd}_2\text{Zr}_2\text{O}_7$). The experiments were carried out within a temperature range of 800–1600°C for a sintering time of 5–50 h, in air and in an oxygen atmosphere. The phase formation conditions in matrices of different compositions are identified. Practical recommendations are issued.

Oxides with a lattice of the fluorite type (cubic zirconium dioxide, zirconolite, pyrochlore) have a high capacity with respect to actinides and high chemical and radiation resistance [1–4]. Therefore, it is advisable to use such phases as matrices, in which waste actinide materials can be shipped to burial or transmutation. This method of utilization of actinides is related to the development of methods of synthesis of such materials. One commonly used method is cold pressing — sintering (CP-S). It was used in the USA to develop a technology of immobilization of so-called “superfluous” plutonium into a titanate with the pyrochlore structure [4]. In optimizing the synthesis parameters it is essential to determine the temperature and duration of the process to ensure the production of a material with the required properties. For this purpose we investigated the kinetics of phase formation with lattices of the zirconolite and pyrochlore types in CP-S synthesis.

The compositions of samples consisted of the following series of elements: Ca–Zr–Ti–O, Ca–Ce–Ti–O, Gd–Ti–O, and Gd–ZrO–O. The target phases were zirconolite (the ideal formula is $\text{CaZrTi}_2\text{O}_7$) or pyrochlore ($\text{CaCeTi}_2\text{O}_7$, $\text{Gd}_2\text{Ti}_2\text{O}_7$, $\text{Gd}_2\text{Zr}_2\text{O}_7$). The initial batches were prepared from carbonate (CaCO_3) and oxides (ZrO_2 , TiO_2 , CeO_2 , Gd_2O_3) crushed in an agate mortar to a size of 20–30 μm . The mixtures were molded under a pressure of 200–400 MPa in the form of tablets of diameter 15–20 mm and height 2–4 mm and sintered in alundum crucibles in a resistance furnace. The experiments were carried out in air and the experiments with the compositions containing cerium were performed as well in an oxygen atmosphere. Alto-

gether more than 100 samples were prepared and analyzed using a Philips PW3040/00 X'Pert MPD diffractometer in the following conditions: CuK_α radiation, voltage 40 kV, current 20–30 mA, angle 2θ ranging from 3 to 65°, measurement step of 0.01–0.02°, and pulse increment in each point lasting from 0.5 to 5 sec. The diffraction patterns were deciphered using the PDF database (JCPDS-ICDD, 1997–1999).

Tables 1–5 list the initial batch compositions, the experiment parameters, and the relative intensities of the main reflections of the phases identified. Samples having the same composition are arranged in order of increasing temperature and duration of sintering. The reflection intensities make it possible to estimate the relative quantities of phases and thus to reveal the effect of the synthesis conditions on the phase composition of the sample.

Ca–Zr–Ti–O system. The target phase for these compositions of the initial batch is zirconolite (the ideal formula is $\text{CaZrTi}_2\text{O}_7$). Zirconolite is not contained in the products of the experiments performed at 800 and 900°C with a sintering duration of 15 h. Instead of zirconolite, titanium oxide (rutile) and zirconium oxide (the monoclinic variety, i.e., baddeleyite) as well as calcium titanate (perovskite) are registered. The oxides most probably are the initial batch components that have not reacted and perovskite is an intermediate product of synthesis. The formation of zirconolite is first registered in samples exposed for 15 h at 1000°C or for 10 h at 1100°C (Table 1).

The interplanar distance of the main reflection is $d_{221} = 0.293–0.294$ nm, which coincides with the standard values. As the sintering temperature and (or) duration increase, the quantity of the target phase grows, and the shares of titanium and zirconium oxides decrease. Zirconolite becomes the leading phase in samples prepared at a tempera-

¹ IGEM of the Russian Academy of Sciences, Moscow, Russia.

² Radon Research and Production Association, Moscow, Russia.

³ KIGAM Co., Korea.

TABLE 1

Number of experiment	Synthesis parameters		Relative intensity of phase reflections			
	temperature, °C	duration, h	rutile	baddeleyite	perovskite	zirconolite
38	800	15	100	54	30	Not identified
39	900	15	100	70	77	The same
1	1000	5	59	100	74	"
40	1000	15	78	100	95	Traces*
93	1000	20	50	100	69	6
2	1050	5	61	100	77	Traces
44	1100	15	61	100	78	27
85	1100	20	49	100	64	25
51	1200	10	88	100	13	90
45	1200	15	58	84	92	100
75	1200	20	57	62	70	100
53	1300	10	29	30	38	100
67	1300	20	Not identified	Traces	Traces	100
94	1400	20	Not identified	The same		100
20	1450	5	The same	"		100
99	1450	20	"	"		100
103	1450	20	"	"		100
101	1450	48	"	"		100
129	1500	5	"	"		100
27	1500	5	"	"		100
14	1500	5	"	"		100
10	1500	5	"	"		100
60	1500	10	"	"		100
120	1500	20	"	"		100
121	1500	20	"	"		100
80	1500	48	"	"		100
105**	1500	20	"	"		100
107**	1500	40	"	"		100
111**	1500	20	"	"		100
18	1550	5	Melting of initial batch			

* Traces: relative intensities of reflection < 5%.

** Material obtained in a previous experiment served as a batch.

ture of 1200°C with a sintering duration of 20 h. However, the content of rutile, baddeleyite, and perovskite in them still remains high. An increase in the temperature to 1300°C with the same exposure results in a sharp decrease in the amount of these phases. With further increase in the temperature (duration of synthesis), the phase composition of samples virtually does not change, which is an evidence of the equilibrium reached in the system. At a temperature of 1300°C, approximately 20 h is required for this. At temperatures of 1450 – 1500°C, the time of reaching the equilibrium is not greater than 5 h. At a temperature of 1550°C, the batch melted, which agrees with the data on the melting point of zirconolite (approximately 1530°C) [5].

The products of the experiments perform at the maximum temperature and maximum sintering duration contain a small quantity of perovskite apart from zirconolite. This is probably related to the difference between the real composi-

tion of zirconolite in the samples and the perfect stoichiometry of $\text{CaZrTi}_2\text{O}_7$, which agrees with the results of studying the compositions of synthetic zirconolite in the $\text{CaO} - \text{ZrO}_2 - \text{TiO}_2$ system [1, 6].

Ca – Ce – Ti – O system. The phase composition of the products of the experiments in this system depends on the sintering duration and temperature, as well as on the oxidation conditions of synthesis. The latter is presumably related to the existence of two degrees of oxidation in cerium: Ce^{3+} and Ce^{4+} , each of them having its own typical set of crystalline phases. Pyrochlore in an oxygen medium at 1100°C is formed in a substantial quantity already after 20 h, although the prevalent phase is cerium dioxide, i.e., cerianite, and a certain quantity of rutile is registered as well (Table 2). With increasing temperature, the share of pyrochlore grows and the content of the other phases decreases. At 1300°C, not more than 20 h is needed for reaching equilibrium. Increase of the sintering duration has virtually no effect on the phase ratio in the end product. Such samples consist of pyrochlore with subordinate quantities of perovskite and cerianite. The main reflection of the principal phase is $d_{222} = 0.2926 - 0.2937$ nm. The possibility of obtaining cerium pyrochlore was discussed earlier [7]. The available x-ray databases do not contain data on pyrochlore $\text{CaCeTi}_2\text{O}_7$. The diffraction pattern of the phase obtained in our experiment is identical to the diffraction pattern of $\text{Tb}_2\text{Ti}_2\text{O}_7$ with the pyrochlore structure.

The values of the interplanar distance of the main reflection of perovskite lie between the standard values for calcium perovskite CaTiO_3 ($d_{121} = 0.270$) and cerium perovskite $\text{Ce}_{0.66}\text{TiO}_{2.975}$ ($d_{110} = 0.273$ nm). Apparently, perovskite in the samples obtained by us is a solid solution of CaTiO_3 and $\text{Ce}_2\text{Ti}_3\text{O}_9$ of the composition $(\text{Ca}_{1-x}\text{Ce}_{0.66x})\text{TiO}_3$. Judging from the data of scanning electron microscopy, it has a rhombic lattice symmetry (spatial group $Pnma$). A clear decrease in the value d of the reflection $hkl = 121$ from 0.2724 nm (1000°C) to 0.2709 – 0.2713 nm (1300 – 1350°C) is registered. The values d of pyrochlore with indexes $hkl = 222$ lie within the range of 0.2926 – 0.2935 nm and do not reveal a clear dependence on the conditions of experiments. The variation of the interplanar distances is presumably related to variations of the chemical compositions of the phases. Repeated firing of samples at a lower temperature does not have a perceptible effect on the interplanar distances of the phases and, accordingly, on their composition.

Ceramics of the $\text{CaCe}_{0.9}\text{Ti}_2\text{O}_{6.8}$ stoichiometry synthesized from the same batch in air has certain distinct features. Substantial quantities of the target phase of pyrochlore exist only in samples obtained at 1200 – 1300°C (Table 3). The quantity of this phase in samples prepared at a temperature below 1200°C is low, presumably due to uncompleted synthesis reactions. As the temperature grows to 1400°C, the quantity of pyrochlore decreases and at 1500°C is not identified. The main phase in these samples is perovskite. The reason for the disappearance of pyrochlore is the reduction of

TABLE 2

Number of experiment	Estimated batch composition	Synthesis parameters		Relative intensity of main phase reflections*			
		temperature, °C	duration, h	rutile	baddeleyite	perovskite	zirconolite
115	CaCe _{0.7} Ti ₂ O _{6.4}	1300	20	Traces	33 (0.2713)**	Traces	100 (0.2935)***
114	CaCe _{0.8} Ti ₂ O _{6.6}	1300	20	Not identified	17	The same	100
126****	The same	1250	50	The same	16 (0.2715)	"	100
123	CaCe _{0.9} Ti ₂ O _{6.8}	1000	20	"	100 (0.2724)	26	16
87	The same	1100	20	15	Not identified	100	30 (0.2929)
77	"	1200	20	16	The same	96	100 (0.2926)
69	"	1300	20	Not identified	13 (0.2711)	5	100 (0.2929)
97	"	1350	20	The same	22 (0.2713)	9	100 (0.2929)
127	CaCeTi ₂ O ₇	1250	50	6	28 (0.2711)	19	100 (0.2934)
106	The same	1270	40	Traces	19	25	100 (0.2927)
130	"	1300	5	The same	25 (0.2709)	34	100 (0.2928)
113	"	1300	20	Not identified	14 (0.2716)	14	100 (0.2935)
128	"	1300	20	The same	13 (0.2714)	12	100 (0.2937)
104	"	1300	20	"	12	9	100 (0.2929)
112	"	1300	20	"	12	11	100 (0.2933)
119****	"	1200	20	"	8 (0.2714)	8	100 (0.2935)
122****	"	1000	20	"	7 (0.2714)	10	100 (0.2934)
109	"	1350	40	"	17	13	100 (0.2931)

* Rutile — TiO₂, perovskite — (Ca, Ce)TiO₃, cerianite — CeO₂, pyrochlore — CaCeTi₂O₇.

** d_{110} perovskite, nm.

*** d_{222} pyrochlore, nm.

**** Material obtained in a previous experiment served as a batch.

cerium to the trivalent state. The same phenomenon was registered before in incorporation of cerium into zirconolite [8].

Apparently, 20 h at 1300°C and not more than 5 h at temperature of 1450 – 1500°C is sufficient to complete the reactions of synthesis in the cerium system in air. Fluctuations in the phase compositions judging from the interplanar distances occur within a narrower range compared with the same compounds obtained in an oxygen medium.

Gd – Ti – O system. The phase composition of the products of experiments in this system is the simplest (Table 4). The pyrochlore phase in a perceptible quantity emerges already at a temperature of 1000°C, although the products of the experiments still retain gadolinium and titanium oxides. As the temperature increases, the pyrochlore content grows, and at a temperature above 1200°C it becomes the only phase. Its diffraction pattern is identical to the pattern of the standard compound Gd₂Ti₂O₇ ($d_{222} = 0.294$ nm). To reach equilibrium, 20 h is needed at 1200°C and not more than 5 h at 1450 – 1500°C.

Gd – Zr – O system. The target phase is cubic oxide Gd₂Zr₂O₇ with a lattice of the pyrochlore type. The phase formation reactions in this system proceed at a very slow rate, the slowest one among the systems considered. After firing for 20 h at a temperature of 1000 – 1100°C, trace quantities of cubic oxide are formed, whereas the main phases are baddeleyite and Gd₂O₃, i.e., the initial batch com-

TABLE 3

Number of experiment	Synthesis parameters		Relative intensity of main phase reflections			
	temperature, °C	duration, h	rutile	baddeleyite	perovskite	zirconolite
91	1000	20	14	Not identified	100	13 (0.2928)*
83	1100	20	16	The same	100	43 (0.2927)
73	1200	20	11	"	51	100 (0.2926)
62	1300	20	Not identified	36 (0.2713)**	10	100 (0.2928)
65	1300	20	The same	42 (0.2715)	8	100 (0.2929)
96	1400	20	"	100 (0.2719)	17	Traces
21	1450	5	"	100 (0.2720)	19	The same
25***	1450	5	"	100 (0.2721)	16	"
11	1500	5	"	100 (0.2719)	18	Not identified
15	1500	5	"	100 (0.2720)	29	The same
81	1500	48	"	100 (0.2719)	24	"

* d_{222} pyrochlore, nm.

** d_{110} perovskite, nm.

*** Preliminary sintering at a temperature of 1000°C for 5 h.

TABLE 4

Number of experiment	Synthesis parameters		Relative intensity of main phase reflections		
	temperature, °C	duration, h	rutile	Gd ₂ O ₃	pyrochlore
92	1000	20	10	100	62
84	1100	20	Traces	11	100
88	1100	20	The same	17	100
74	1200	20	Not identified		100
78	1200	20	The same		100
63	1300	20	"		100
66	1300	20	"		100
70	1300	20	"		100
22	1450	5	"		100
12	1500	5	"		100
16	1500	5	"		100

ponents (Table 5). As the temperature grows, the content of the target phase increases; however, even after 5 h of sintering at 1500–1550°C this phase is not yet the prevailing one. The samples preserve perceptible quantities of baddeleyite and Gd₂O₃, and tetragonal ZrO₂ is registered as well. Only after the maximum duration (50 h) and the maximum temperature (1600°C) of the experiments does the (Gd, Zr) oxide become the only phase. Its diffraction pattern clearly exhibits the reflections typical of the pyrochlore structure.

Consequently, the phase composition of the samples depends on the conditions of their production. The products of relatively low-temperature and short experiments contain a substantial quantity of the initial batch components (zirconium, titanium, and gadolinium oxides) and the intermediate phases (perovskite, tetragonal zirconium dioxide). As the sintering duration increases, their content decreases, and the amount of the target phase increases. Starting with a certain moment, an increase in the sintering duration (at a constant temperature) does not modify the phase composition of the samples. This suggests that an equilibrium state is achieved. The time of reaching the equilibrium becomes shorter with increasing sintering temperature. For the CaO–TiO₂–ZrO₂ system, 20 h is required at a temperature of 1300°C and 5 h at temperatures of 1450–1500°C. In the case of the cerium-bearing system, this requires more than 50 h at 1250°C, 40 h at 1270°C, and 20 h at 1300–1350°C (experiments in an oxygen medium and in air). Equilibrium in air at temperatures of 1450–1550°C is reached already after 5 h. For the Gd₂O₃–TiO₂ system, about 20 h is required at 1200–1300°C and not more than 5 h at 1450–1500°C. The slowest phase formation processes are observed in the Gd₂O₃–ZrO₂ system, which required 50 h even at the maximum temperature of 1600°C to complete the synthesis. The products of the experiments performed in this system at lower temperatures contain a large quantity of initial components.

The difference in the reaction rates is probably related to different chemical properties of the elements and their com-

TABLE 5

Number of experiment	Synthesis parameters		Relative intensity of main phase reflections			
	temperature, °C	duration, h	baddeleyite	Gd ₂ O ₃	tetragonal ZrO ₂	Zr ₂ Gd ₂ O ₇
90	1000	20	65	100	Not identified	
82	1100	20	48	100	Not identified	Traces
86	1100	20	44	100	The same	The same
72	1200	20	24	100	13	23
68	1300	20	19	100	61	76
64	1300	20	19	100	63	78
23	1450	5	26	100	29	62
26*	1450	5	17	100	36	51
13	1500	5	20	100	97	79
17	1500	5	13	100	68	94
19	1550	5	7	66	100	73
110	1550	48	Not identified			100
125**	1600	50	The same			100

* Preliminary sintering at a temperature of 1000°C for 5 h.

** Material obtained in experiment 13 served as a batch.

pounds. Titanium and zirconium are located in subgroup IVb of the Periodic Table. Their ions in the maximum degree of oxidation (+4) have the *d*⁰ configuration. Zirconium manifests more perceptible metallic properties, and the size of the Zr⁴⁺ ion is larger than that of Ti⁴⁺. This determines the different coordination environment of their ions and different strength of their bond with the anions in the crystalline lattice [9].

The phase composition of samples in the state of equilibrium is affected by the temperature as well as the redox conditions of their synthesis. The later is especially typical of the cerium-bearing samples, in which, depending on the temperature and atmosphere of synthesis, the leading phase is pyrochlore (in an oxygen medium and in air at moderate temperatures) or perovskite (high-temperature experiments in air). This is related to the transformation of the main part of cerium into the trivalent state. According to the obtained data, this transformation presumably takes place within a temperature range between 1300 and 1400°C.

The samples in the state of equilibrium exhibit different numbers of phases: one (Gd₂O₃–TiO₂ and Gd₂O₃–ZrO₂), two (CaO–TiO₂–ZrO₂), or three (CaO–Ce₂O₃–CeO₂–TiO₂) phases. Note that even samples whose composition correlates with the ideal formula of zirconolite CaZrTi₂O₇ or cerium pyrochlore CaCeTi₂O₇ contain other phases besides the target compound. This is due to the difference between the actual composition and the nominal phase stoichiometry. It is known that the compositions of synthesized zirconolite ceramics correlate with the generalized formula of CaZr_xTi_{3–x}O₇, where *x* varies from 0.8 to 1.37 [1]. The same fact probably accounts for the emergence of other phases along with pyrochlore in the matrix corresponding to the formula of CaCeTi₂O₇. An analysis of published data indicated

that pyrochlore titanate as a rule has an excess of calcium ions over actinide ions compared with the ideal formula [10]. The actual formula of these phases can be written as $\text{Ca}_{1+x}(\text{An}, \text{Ce})_{1-x}\text{Ti}_2\text{O}_{7-x}$, where x varies from 0 to 0.2. The special interest in studying cerium samples is due to the similar behavior of this element and plutonium in crystalline matrices [7, 8]. None of the cerium sample had the CeTi_2O_6 phase of the brannerite type, although such compounds are quite typical of actinides [10].

The maximum number of phases in each system under equilibrium conditions is determined by the Gibbs rule. Under constant temperature and pressure it is equal to the number of components. In our case it is equal to two ($\text{Gd}_2\text{O}_3 - \text{TiO}_2$, $\text{Gd}_2\text{O}_3 - \text{ZrO}_2$), three ($\text{CaO} - \text{ZrO}_2 - \text{TiO}_2$), or four ($\text{CaO} - \text{CeO}_2 - \text{Ce}_2\text{O}_3 - \text{TiO}_2$). The heterovalent cerium oxides should be regarded as separate components, since each of them has its own set of corresponding phases. In none of the samples considered did the number of phases reach the maximum possible value.

Based on the obtained results, the following conclusions can be made. The phase formation reactions in matrices of different compositions at the same temperature proceed at different rates. This process is fastest in the gadolinium-titanium system and slowest in the gadolinium-zirconium system. The reaction rate in the $\text{Ca} - \text{Zr} - \text{Ti} - \text{O}$ and $\text{Ca} - \text{Ce} - \text{Ti} - \text{O}$ systems is of an intermediate value. Equilibrium in titanate ceramics is reached at $1400 - 1500^\circ\text{C}$ already after 5 h, whereas the $\text{Gd} - \text{Zr} - \text{O}$ system requires an order of magnitude longer time. This is presumably one of the reasons why USA researchers select pyrochlore with a formula of $(\text{Ca}, \text{Gd}, \text{U}, \text{Pu})_2(\text{Hf}, \text{Ti})_2\text{O}_7$ as a matrix for immobilization of plutonium [4]. Zirconate pyrochlore is more stable than titanate pyrochlore [3]. It can be produced by melting with subsequent crystallization [11]. Another method consists in increasing the homogeneity of the batch by replacing oxide mixtures by sol-gel mixtures [1]. The process of synthesis can be accelerated by introducing dopants. In particular, a TiO_2 additive makes it possible to obtain pyrochlore $\text{Gd}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ in a shorter time without significantly decreasing the strength properties of the matrix.

Since cerium exists in two valence forms, the equilibrium phase composition of cerium ceramics depends on the temperature and the oxidation conditions of synthesis. The production of pyrochlore is possible in an oxygen medium or in air at a temperature not higher than 1300°C . At a higher temperature cerium passes to the trivalent state, which leads to destabilizing of pyrochlore and the formation of perovskite $(\text{Ca}_{1-x}\text{Ce}_{0.66x})\text{TiO}_3$. A similar behavior of plutonium was registered in crystalline matrices [8]. The trivalent

cerium ion is more stable than Pu^{3+} . In other words, other conditions being equal, the $\text{Ce}^{3+} : \text{Ce}^{4+}$ ratio in matrices of similar compositions is higher than the $\text{Pu}^{3+} : \text{Pu}^{4+}$ ratio. Consequently, the properties of cerium ceramics produced in air should be similar to the properties of plutonium-containing samples produced in the reducing condition of synthesis. The results of studying the cerium-containing phases synthesized in an oxidizing atmosphere can be used to understand the behavior of plutonium ceramics sintered in air.

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